Citrus Crop Sampling & Analysis Report
Cawelo Water District
Bakersfield, California

Prepared by:

Enviro-Tox Services, Inc.
20 Corporate Park, Suite 220
Irvine, California 92606

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This report pertains to the evaluation of citrus crops irrigated with water supplied by the Cawelo Water District (the District). Enviro-Tox Services, Inc. (Enviro-Tox) prepared this report for the exclusive use of the District. Enviro-Tox's professional services have been performed using that degree of care and skill ordinarily exercised under similar circumstances by other scientists and engineers practicing in this field. No other warranty, expressed or implied, is made as to the professional advice presented in this report.

This report has been prepared by Dr. Heriberto Robles of Enviro-Tox. Dr. Robles is a Diplomate of the American Board of Toxicology (DABT) with 35 years of experience in environmental toxicology and human health and environmental risk assessment for industrial, real estate, and governmental clients. Dr. Robles has conducted, managed, and/or collaborated on numerous risk assessment projects at many sites including mining and military facilities, proposed public school sites, hazardous waste landfills, and oil fields, as well as commercial and industrial facilities. Examples of Dr. Robles' work include the evaluation of health hazards associated with the presence of PCBs, radionuclides, perchlorate, dioxins/furans, petroleum hydrocarbons, volatile and semivolatile organics, polycyclic aromatics, chlorinated solvents, pesticides, asbestos and metals in environmental media. Dr. Robles has also conducted health risk assessments for human exposure to bio-aerosols, radon gas and electromagnetic fields. He has conducted toxicological evaluations of environmental and industrial chemicals and has communicated risk information to regulatory agencies and the general public.

Heriberto Robles, M.S., Ph.D., D.A.B.T.
Board Certified Toxicologist
Enviro-Tox Services, Inc.

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Background

Cawelo Water District (Cawelo), a public water agency located in Bakersfield, California and serving Kern County landowners, has commissioned Enviro-Tox Services, Inc. (Enviro-Tox) to review and analyze water quality and food crop data. The objective of the review is to assess the safety of blended produced water for agricultural irrigation purposes. This ongoing testing program, which adheres to testing protocols established by the U.S. Environmental Protection Agency, is a voluntary and collaborative effort undertaken by Cawelo with results provided to the Central Valley Regional Water Quality Control Board, the regulator charged with ensuring water quality and safety.

Initial Water Quality Study Findings:
Organic compounds within safe drinking water quality standards and Cawelo's produced water supply safe for agricultural use.

In November 2015, Cawelo proactively engaged Enviro-Tox to first analyze water quality testing data – specifically studying the levels of organic compounds in its blended produced irrigation water. For background, Cawelo describes its produced water as water that is thoroughly treated and monitored by oil producers and based on its quality, is provided to Cawelo for agricultural use. Cawelo also notes that when it receives produced water, it is blended with water from other groundwater and surface water sources and tested before being provided to farmers to use in agriculture. Results from Cawelo's initial water quality testing were submitted to the Regional Board in April 2016. That initial report concluded that Cawelo's blended produced water supply met all applicable regulatory standards for agricultural use – all organic compounds were either at or below levels considered safe for drinking water.

Initial testing of almonds, grapes and pistachios was also presented at that time and showed no cause for concern when comparing crops irrigated with blended produced water against the same commodities irrigated with other water sources.

To ensure a complete review, Cawelo has engaged Enviro-Tox to conduct ongoing analysis of additional crops as they come into season. Specifically, to determine whether chemical constituents in irrigation water are absorbed and accumulate, also known as plant uptake, into the fruit. This Citrus Crop Sampling and Analysis Report (the Report) is now the third wave of testing included in this ongoing series. As each report becomes available, it will be provided to the Regional Board for review and analysis.

Citrus Sampling and Analysis Report

The Report is an independent review and evaluation of citrus crop analytical data – comparing crops irrigated with Cawelo's blended produced water supply against crops irrigated with water from other sources. Cawelo's water supply sources include the Kern River, State Water Project, pumped groundwater, and produced water generated from oil production operations, which is filtered, treated and then blended with other water supplies.

The Report specifically looked for nine indicator chemicals in citrus fruits (mandarins, oranges and lemons) irrigated with Cawelo's blended produced water supply. An indicator chemical is defined in the Report as a chemical that was detected in Cawelo's initial water quality study. Of note, all nine chemicals identified in the water quality study were found at levels below established drinking water quality standards. The indicator chemicals studied in this Report include: acetone and the petroleum-derived chemicals benzene, toluene, ethylbenzene, xylenes, acenaphthene, fluorene, naphthalene and phenanthrene.

For this Report, crop samples irrigated with Cawelo's blended produced water supply are defined as the "Test" samples, while crop samples irrigated with water from other sources are defined as the "Control" samples. Test and Control sample crops were selected based on what was in season, which is why mandarins, oranges and lemons were collected from eighteen different sampling locations on February 16 and 17, 2016.

Report Findings

Initial testing results indicate that citrus crops irrigated with Cawelo's blended produced water supply are safe for consumption. This is a preliminary conclusion based on the available citrus data.

Initial Report Findings:
Mandarins, oranges and lemons irrigated with Cawelo's blended produced water supply safe for consumption.

Except for one (details below), the indicator chemicals studied were either not found in the crop samples or were found at similar concentrations in both the Test and Control samples. These results indicate that organic chemical constituents in blended produced water are not being absorbed nor accumulate in edible fruit. Continuing crop and water testing is recommended as additional crops irrigated with Cawelo's blended produced water supply come into season.

Report Conclusions

When reviewing the findings, it is important to note that the Report's indicator chemicals are not unique to blended produced water and are common chemicals found in our everyday environment. For this reason, ongoing testing is recommended to rule out false positives as a result of contamination from other sources. It is also recommended that future Test and Control samples be collected away from known external sources of petroleum-derived chemicals or combustion products such as roads or highways. Following is a summary of the indicator chemicals studied in the Report and the conclusions drawn from our data review:

- Acetone: Crops in both the Test and Control samples showed very similar levels of acetone, illustrating that acetone is a naturally occurring substance and not a result of irrigation water.
- Benzene: Crops in both the Test and Control samples did not show the presence of benzene.
- Toluene: Crops in both the Test and Control samples did not show the presence of toluene.

- Ethylbenzene: Crops in both the Test and Control samples did not show the presence of ethylbenzene.

- Xylenes: Crops in both the Test and Control samples did not show the presence of xylenes.

- Acenaphthene: Crops in both the Test and Control samples did not show the presence of acenaphthene.

- Fluorine: Crops in both the Test and Control samples did not show the presence of fluorine.

- Naphthalene: Crops in both the Test and Control samples did not show the presence of naphthalene.

- Phenanthrene: Two of the nine Test samples showed extremely low concentrations of phenanthrene. Additional samples were collected from the same locations for follow-up testing and did not show the presence of phenanthrene, indicating the possibility that the first two samples were false positives as a result of external contamination (most likely airborne). Phenanthrene, which is produced from the combustion of fossil fuels, can commonly be found in dust particles near roads, chimneys and internal combustion engines. It is one of the major organic contaminants produced by domestic wood burning and road traffic. It is likely the detected phenanthrene originated from combustion engine emissions. However, the source cannot be definitively confirmed at this time and further tests are recommended.

Phenanthrene is a common air contaminant from the Polycyclic Aromatic Hydrocarbon (PAH) family and known to be easily absorbed by plants and fruits. Airborne PAHs at the Test and Control fields were not tested in this Report. Given that the majority of the original samples and follow-up samples did not show the presence of phenanthrene, it cannot be determined at this time the source of this particular chemical, as a host of possibilities exist due to the everyday presence of phenanthrene in the environment.

Ongoing Crop Testing Program

To date, this is the third round in a series of tests examining Cawelo’s blended produced water supply. While initial water quality testing results and the subsequent citrus fruit analysis indicate that Cawelo’s blended produced water supply is safe for agricultural irrigation, ongoing testing and collaboration between Cawelo and the Regional Board is recommended. Conclusions to date are preliminary and Enviro-Tox recommends continued testing as additional crops come into season.

1.0 Introduction

Enviro-Tox Services, Inc. (Enviro-Tox) has prepared this Citrus Crop Sampling and Analysis report (the Report) for the Cawelo Water District (the District) of Bakersfield, California. The Report describes the independent review and evaluation of citrus crop analytical data performed by Enviro-Tox, a qualified environmental firm that specializes in Environmental Toxicology and Human Health and Ecological Risk Assessment.

32,000 acre-feet of produced water equals:

- 10.4 billion gallons per year
- 28.57 million gallons per day
- 840 gallons per irrigated acre per day

The District, located just north of Bakersfield, California, provides irrigation water to approximately 34,000 acres of orchards, vineyards, and other crops. The District receives approximately 32,000 acre-feet (10.4 billion gallons) of water a year from regional oil producers. Every barrel of oil produced at the Kern River Oil Field generates approximately 15 barrels (630 gallons) of water. The water that results from the extraction of oil from local oil wells is called produced water. Produced water is treated by oil extraction companies, filtered and then delivered by pipeline to the District, where it is blended with other water supplies and provided for irrigation uses.

Produced water is known to contain traces of petroleum hydrocarbons, as documented in Amec Foster Wheeler Environmental & Infrastructure, Inc.'s report (Amec; 2015). According to Amec's report, traces of petroleum hydrocarbons were observed in water samples collected at one location within the Kern River Oil Field (Station 36 water plant) and four locations within the Cawelo Ponds. Water quality analytical results reported by Amec are summarized in Table 1. Organic chemical concentrations detected by Amec in the water samples were very low, in parts per million and parts per billion range. In fact, organic chemical concentrations detected in the pond outflow were all within levels considered acceptable for drinking water (Enviro-Tox 2016).

The objectives of Cawelo's Citrus Crop Sampling and Analysis program were to:

- Determine whether petroleum-derived chemicals known to be present in the produced water are possibly accumulating in edible tree fruit irrigated with blended produced water;

- Assess the potential for translocation of petroleum-derived chemicals from irrigation water to edible fruits;
- Obtain data to supplement existing information related to the behavior of petroleum hydrocarbon residues in irrigation water. This data will be used to better understand chemical migration pathways;
- Provide data for possible future human health risk assessment studies; and
- Use data obtained to determine if it is indeed safe to use blended produced water for the irrigation of edible tree fruit.

2.0 Citrus Crop Sample Collection and Analysis

On February 15 and 16, 2016, Advanced Environmental Concepts, Inc. of Bakersfield, California (an independent third-party sampling firm) collected citrus crop samples from eighteen sampling locations. The citrus crop samples were collected from local agricultural fields irrigated with water provided by the District and from control fields.

The control field samples were collected from citrus crop fields not irrigated with produced water. Specifically, the control field samples were collected from Kern and Tulare County orchards that are not irrigated with water provided by the District or water originating from oil extraction facilities. In this report, citrus crop samples collected from fields irrigated with District-supplied water are called "Test" samples; citrus crop samples collected from fields irrigated with water provided by other water suppliers are named "Control" samples. Nomenclature for the Test and Control samples was sequential so the testing laboratories could not identify whether a particular sample originated at a Test or Control location. Test and Control sampling locations are presented in Figure 1.

2.1 Analysis

Weck Laboratories, Inc., a California state-certified analytical laboratory, analyzed Test and Control citrus crop samples for selected petroleum-derived volatile organic compounds (VOCs) and semivolatile organic compounds (SVOCs). The VOCs were analyzed using U.S. Environmental Protection Agency (U.S. EPA) Method 8260B. For SVOCs, samples were analyzed using U.S. EPA Method 8270C-SIM. Test and Control citrus crop samples analyzed for VOCs and SVOCs were collected, preserved and analyzed in accordance with U.S. EPA protocols. The analytes selected for this study are the same analytes reportedly present in produced water (Table 1). Citrus crop analytical results for VOCs and SVOCs are presented in Table 2. Copies of the Weck Laboratories analytical reports are included in Appendices A and B.

In addition to the samples analyzed for VOCs and SVOCs, citrus crop samples were also collected to analyze the presence of oils and fatty acids. A set of citrus crop samples from the Test and Control fields was analyzed for total saturated and unsaturated fatty acids using Analytical Method AOAC Official Method 996.06. The analysis was conducted by Anresco

Laboratories of San Francisco, California (Anresco). Citrus crop analytical results for oils and fatty acids are presented in Table 3. A copy of Anresco's report is included in Appendix C.

2.2 Indicator Chemicals

According to Amec's 2015 report, chemicals detected in produced water included acetone and the petroleum-derived benzene, toluene, ethylbenzene, xylenes, acenaphthene, fluorene, naphthalene and phenanthrene (Table 1). Since these nine chemicals have been positively identified in produced water, these same nine chemicals were used in this study as "indicator" chemicals for produced water.

By definition, a "indicator" compound is a substance that is known to be present at a Point A and can be used to trace (follow) the chemical migration through the environment to a final destination, or Point B. An ideal indicator compound is one that is not found in the environment and that can only be found at the source in Point A. For this study none of the chemicals identified in the produced water can be deemed to be an ideal indicator compound since all nine chemicals are either naturally occurring or common environmental contaminants and are not unique to Cawelo Water Ponds.

2.3 Confirmation Sampling

Analytical results for citrus crop samples collected at Test sampling locations TF-7 and TF-8 (Figure 1) revealed the presence of low concentrations of phenanthrene (Table 2). No other petroleum-hydrocarbon indicator chemical was detected in any of the Test or Control samples (Tables 2 and 4). In light of these results, Dr. Heriberto Robles visited sampling locations TF-7 and TF-8 on March 23, 2016. The objectives of the visit were to (1) collect new citrus crop samples that could be used to corroborate the results obtained from prior sampling; (2) look for possible external sources of phenanthrene contamination in the vicinity of sampling locations TF-7 and TF-8; and (3) collect dust samples around sampling locations TF-7 and TF-8 to see if phenanthrene is present in surface dust in the vicinity of the sampling locations. Crop sample TF-10 was collected to serve as confirmation sample for sampling location TF-8. Crop sample TF-11 was collected to serve as confirmation sample for sampling location TF-7. Both confirmation samples were collected from the same fields as the original samples. Analytical results for confirmation samples TF-10 and TF-11 are presented in Table 4. The significance of the results obtained from the citrus crop sampling and analysis is discussed in the following sections.

Table 1. Water Quality Analytical Results Summary: Volatile Organic Compounds, Semivolatile Organic Compounds, and Total Petroleum Hydrocarbons

Well/Sample ID	Sample ID	Volatile Organic Compounds[1] (ug/L)							Polycyclic Aromatic Hydrocarbons[2] (ug/L)								TPH[3] (mg/L)
		Acetone	Benzene	Ethyl-benzene	m,p-Xylene	o-Xylene	Toluene	Total Xylenes	Acenaphthene	Acenaphthylene	Chrysene	Fluorene	Naphthalene	Phenanthrene	Pyrene	
Plant 36	W039	31	0.47 J	0.71	2.6	1.3	0.67	3.9	0.63	<0.098	<0.098	0.37	0.11 J	0.38	<0.098	0.12
Polish Pond	W042	86	0.33 J	0.39 J	1.3	0.74	0.49 J	2.0	0.53	<0.097	<0.097	0.29	0.11 J	0.27	<0.097	0.19
Polish Pond	W043[4]	100	0.31 J	0.38 J	1.2	0.59	0.47 J	1.8	0.57	<0.097	<0.097	0.35	0.12 J	0.28	<0.097	0.097
Reservoir B	W044	150	<0.25	0.25 J	0.75 J	0.43 J	0.39 J	1.2	0.49	<0.097	<0.097	0.50	<0.097	0.29	<0.097	0.15
Reservoir B Outflow	W045	50	<0.25	<0.25	<0.50	<0.25	<0.25	<0.50	<0.096	<0.096	<0.096	<0.096	<0.096	<0.096	<0.096	0.080

Notes:

1. Volatile organic compounds analyzed using U.S. EPA Method 8260B.
2. Polycyclic aromatic hydrocarbons analyzed using U.S. EPA Method 8270C SIM.
3. Total Petroleum Hydrocarobns (TPH; carbon range C29-C40) analyzed using U.S. EPA Method 8015B.
4. Duplicate sample of W042.

Abbreviations:

< = less than the Reporting Limit.
J = result is less than the RL but greater than or equal to the MDL and the concentration is an approximate value
TPH = total petroleum hydrocarbons
ug/L = micrograms per liter

Table 2. Citrus Crop Analytical Results Summary: Volatile Organic Compounds and Semivolatile Organic Compounds

Sample ID	Sample ID	Volatile Organic Compounds[1] (ug/Kg)						Polycyclic Aromatic Hydrocarbons[2] (ug/Kg)			
		Acetone	Benzene	Ethyl-benzene	m,p-Xylene	o-Xylene	Toluene	Acenaphthene	Fluorene	Naphthalene	Phenanthrene
Test Sampling Locations											
TF-HC-1-Lemon-OF-80	TF-HC-1	580	ND<100	ND<100	ND<100	ND<100	ND<100	ND<60	ND<60	ND<60	ND<60
TF-HC-2-Man-CF-320S	TF-HC-2	100	ND<100	ND<100	ND<100	ND<100	ND<100	ND<72	ND<72	ND<72	ND<72
TF-HC-2A-Man-CF-320S	TF-HC-2A	ND<100	ND<100	ND<100	ND<100	ND<100	ND<100	ND<73	ND<73	ND<73	ND<73
TF-HC-3-Man-CF-163	TF-HC-3	ND<100	ND<100	ND<100	ND<100	ND<100	ND<100	ND<66	ND<66	ND<66	ND<66
TF-HC-4-NAV-Zerker	TF-HC-4	ND<60	ND<100	ND<100	ND<100	ND<100	ND<100	ND<68	ND<68	ND<68	ND<68
TF-HC-5-Lem-Resc	TF-HC-5	280	ND<100	ND<100	ND<100	ND<100	ND<100	ND<71	ND<71	ND<71	ND<71
TF-HC-6-Nav-Hillcrest N	TF-HC-6	ND<100	ND<100	ND<100	ND<100	ND<100	ND<100	ND<62	ND<62	ND<62	ND<62
TF-HC-7-Lem-Sherwood	TF-HC-7	220	ND<100	ND<100	ND<100	ND<100	ND<100	ND<68	ND<68	ND<68	130
TF-HC-8-Nav-No. Slope	TF-HC-8	ND<100	ND<100	ND<100	ND<100	ND<100	ND<100	ND<73	ND<73	ND<73	120
TF-HC-9-Man-65	TF-HC-9	120	ND<100	ND<100	ND<100	ND<100	ND<100	ND<70	ND<70	ND<70	ND<70
Control Sampling Locations											
CF-HC-1-Nav-MarRiver-BLK 1	CF-HC-1	ND<93	ND<93	ND<93	ND<93	ND<93	ND<93	ND<68	ND<68	ND<68	ND<68
CF-HC-1A-Nav-MarRiver-BLK 1	CF-HC-1A	ND<96	ND<96	ND<96	ND<96	ND<96	ND<96	ND<69	ND<69	ND<69	ND<69
CF-HC-2-Lem-MarRiver-BLK 2A	CF-HC-2	400	ND<92	ND<92	ND<92	ND<92	ND<92	ND<70	ND<70	ND<70	ND<70
CF-HC-3-Man-MarRiver-BLK 3	CF-HC-3	ND<95	ND<95	ND<95	ND<95	ND<95	ND<95	ND<70	ND<70	ND<70	ND<70
CF-HC-4-Lem-SV2-BLK 1	CF-HC-4	470	ND<97	ND<97	ND<97	ND<97	ND<97	ND<72	ND<72	ND<72	ND<72
CF-HC-5-Nav-SV2-BLK 3	CF-HC-5	94	ND<94	ND<94	ND<94	ND<94	ND<94	ND<64	ND<64	ND<64	ND<64
CF-HC-6-Man-Sunland-BLK 10	CF-HC-6	ND<100	ND<97	ND<97	ND<97	ND<97	ND<97	ND<72	ND<72	ND<72	ND<72
CF-HC-7-Lem-Sunland-BLK 11	CF-HC-7	320	ND<100	ND<100	ND<100	ND<100	ND<100	ND<63	ND<63	ND<63	ND<63
CF-HC-8-Man-Loma-Blk 40	CF-HC-8	180	ND<95	ND<95	ND<95	ND<95	ND<95	ND<70	ND<70	ND<70	ND<70
CF-HC-9-Nav-Loma-Blk 44	CF-HC-9	ND<95	ND<95	ND<95	ND<95	ND<95	ND<95	ND<63	ND<63	ND<63	ND<63

Notes:

1. Volatile organic compounds analyzed using U.S. EPA Method 8260B.
2. Polycyclic aromatic hydrocarbons analyzed using U.S. EPA Method 8270C SIM.

Abbreviations:

< = less than the Reporting Limit.

ug/Kg = micrograms per Kilogram

Table 3. Citrus Crop Analytical Results Summary: Oils and Fats

Sample ID	Sample ID	Percent							
		Total Fat	Saturated Fat	Monounsaturated Fat	Polyunsaturated Fat	Omega-3 Fat	Omega-6 Fat	Omega-9 Fat	Trans Fat
Test Sampling Locations									
TF-FA-1-Lemon-OF-80	TF-FA-1	0.27	0.07	0.05	0.15	0.04	0.11	0.04	0.00
TF-FA-2-Man-CF-320S	TF-FA-2	0.18	0.05	0.04	0.10	0.02	0.07	0.02	0.00
TF-FA-2A-Man-CF-320S	TF-FA-2A	0.16	0.04	0.04	0.08	0.02	0.06	0.02	0.00
TF-FA-3-Man-CF-163	TF-FA-3	0.17	0.05	0.04	0.09	0.02	0.07	0.02	0.00
TF-FA-4-NAV-Zerker	TF-FA-4	0.19	0.05	0.04	0.10	0.02	0.08	0.03	0.00
TF-FA-5-Lem-Resc	TF-FA-5	0.23	0.06	0.04	0.13	0.04	0.09	0.03	0.00
TF-FA-6-Nav-Hillcrest N	TF-FA-6	0.19	0.05	0.03	0.11	0.04	0.08	0.01	0.00
TF-FA-7-Lem-Sherwood	TF-FA-7	0.25	0.07	0.05	0.14	0.04	0.10	0.04	0.00
TF-FA-8-Nav-No. Slope	TF-FA-8	0.17	0.04	0.03	0.10	0.02	0.07	0.01	0.00
TF-FA-9-Man-65	TF-FA-9	0.18	0.05	0.03	0.10	0.02	0.08	0.01	0.00
Control Sampling Locations									
CF-FA-1-Nav-MarRiver-BLK 1	CF-FA-1	0.20	0.05	0.04	0.11	0.03	0.08	0.01	0.00
CF-FA-1A-Nav-MarRiver-BLK 1	CF-FA-1A	0.12	0.03	0.02	0.06	0.02	0.05	0.01	0.00
CF-FA-2-Lem-MarRiver-BLK 2A	CF-FA-2	0.12	0.03	0.02	0.07	0.02	0.05	0.02	0.00
CF-FA-3-Man-MarRiver-BLK 3	CF-FA-3	0.11	0.03	0.02	0.06	0.01	0.05	0.01	0.00
CF-FA-4-Lem-SV2-BLK 1	CF-FA-4	0.08	0.02	0.01	0.05	0.01	0.04	0.01	0.00
CF-FA-5-Nav-SV2-BLK 3	CF-FA-5	0.08	0.02	0.02	0.04	0.01	0.03	0.01	0.00
CF-FA-6-Man-Sunland-BLK 10	CF-FA-6	0.08	0.02	0.02	0.04	0.01	0.03	0.01	0.00
CF-FA-7-Lem-Sunland-BLK 11	CF-FA-7	0.19	0.05	0.04	0.10	0.03	0.07	0.03	0.00
CF-FA-8-Man-Loma-Blk 40	CF-FA-8	0.10	0.03	0.02	0.05	0.01	0.04	0.01	0.00
CF-FA-9-Nav-Loma-Blk 44	CF-FA-9	0.12	0.03	0.02	0.07	0.02	0.05	0.01	0.00

Notes:

Table 4. Citrus Crop Confirmation Sample and Dust Test Analytical Results

		Volatile Organic Compounds[1] (ug/Kg)						Polycyclic Aromatic Hydrocarbons[2] (ug/Kg)			
Sample ID	**Sample ID**	**Acetone**	**Benzene**	**Ethyl-benzene**	**m,p-Xylene**	**o-Xylene**	**Toluene**	**Acenaphthene**	**Fluorene**	**Naphthalene**	**Phenanthrene**
Test Sampling Locations											
TF-HC-7-Lem-Sherwood	TF-HC-7	220	ND<100	ND<100	ND<100	ND<100	ND<100	ND<68	ND<68	ND<68	130
TF-HC-8-Nav-No. Slope	TF-HC-8	ND<100	ND<100	ND<100	ND<100	ND<100	ND<100	ND<73	ND<73	ND<73	120
TF-HC-10-Nav. No. Slope	TF-HC-10	130	ND<23	ND<23	ND<23	ND<23	ND<23	ND<120	ND<62	ND<120	ND<62
TF-HC-11-Lem-Sherwood	TF-HC-11	540	ND<24	ND<24	ND<24	ND<24	ND<24	ND<130	ND<66	ND<130	ND<66
Surface Wipe Samples											
TF-W-01	TF-W-01	220	ND<100	ND<100	ND<100	ND<100	ND<100	ND<140	ND<72	ND<140	ND<72
TF-W-02	TF-W-02	ND<100	ND<100	ND<100	ND<100	ND<100	ND<100	ND<140	ND<71	ND<140	ND<71
TF-W-03	TF-W-03	ND<96	ND<96	ND<96	ND<96	ND<96	ND<96	ND<140	ND<69	ND<140	ND<69

Notes:

1. Volatile organic compounds analyzed using U.S. EPA Method 8260B.
2. Polycyclic aromatic hydrocarbons analyzed using U.S. EPA Method 8270C SIM.

Abbreviations:

< = less than the Reporting Limit.

ug/Kg = micrograms per Kilogram

3.0 Acetone

Acetone was detected in seven of the twelve citrus samples collected from the Test fields and in five of the ten samples collected from the Control fields (Tables 2 and 4). It is not unusual to find acetone in fruit and plant tissues. Acetone is a naturally occurring compound produced by humans, animals, plants, and algae (Elis, et al., 2012). Acetone is soluble in water and has been detected in smoke from volcanoes and forest fires and the burning of tobacco, wood, fuels, and other materials (Hazardous Substances Database [HSDB] 2016).

Since acetone was detected in both Test and Control fruit samples, the sampling results were statistically analyzed to determine if there are any significant differences between the two datasets. The technical aspects of the statistical analysis are described in the following section. The results of the analysis support the conclusion that acetone is of natural origin and is not related to the source of irrigation water.

3.1 Statistical Analysis

The comparison of Test versus Control sampling results is an integral and customary component of most chemical uptake studies. When enough Test and Control analytical data are available, it is recommended to use two-sample tests to perform Test versus Control comparisons. Parametric and nonparametric procedures (hypotheses testing) can be used to compare the measures of central tendencies of the two populations (Test versus Control) when enough data are available from the two populations under consideration. Acetone concentrations reported for the citrus crops collected at the Test and Control fields are presented in Tables 2 and 4.

For this comparison, the Wilcoxon-Mann-Whitney test (WMW; Singh and Maichle, 2013) test was used. In all cases, the tests employed a Type I error rate of 0.05. The WMW test is a nonparametric test used for determining whether a difference exists between the Test and the Control population distributions. The WMW test is used to assess whether or not measurements from one population consistently tend to be larger (or smaller) than those from the other population based upon the assumption that the dispersion of the two distributions are roughly the same. This test determines which distribution is higher by comparing the relative ranks of the two data sets when the data from both sources are sorted into a single list. It is assumed that any difference between the Test and Control concentration distributions is due to a shift in location (mean, median) of the Test concentrations to higher values (due to the possible chemical uptake of the Test subjects).

The statistical test was conducted using the ProUCL 5.0 software (Singh and Maichele, 2013). The null and alternate hypothesis tests were:

H0: the mean acetone concentration for the Test citrus crops is less than or equal to the mean acetone concentration in the Control population.

HA: the mean acetone concentration for the Test samples is greater than the mean acetone concentration in the Control population.

A copy of ProUCL printout is presented in Appendix D. According to the WMW test, there are no statistically significant ($p < 0.05$) differences in the acetone concentrations between samples collected from the Test fields and those collected from the Control fields. Results of the WMW test are presented in Appendix D. The results of the statistical analysis support the conclusion that acetone is of natural origin and is not related to the source of irrigation water.

4.0 Petroleum Hydrocarbons

The introduction of water derived from oil extraction activities into irrigation water systems has generated questions about the possible presence of petroleum-derived chemical residues in the produced water. The purpose of this study was to collect data that would aid in the evaluation of the possible translocation of petroleum hydrocarbons from produced water to edible crops. For this study, citrus crops irrigated with blended produced water were analyzed for chemicals previously identified in produced water (i.e., "indicator" chemicals). The indicator chemicals used in this study included benzene, toluene, ethylbenzene, xylenes, acenaphthene, fluorene, naphthalene and phenanthrene (Table 1). Out of the eight petroleum-derived chemicals analyzed, the only chemical detected in two of the Test crop samples was phenanthrene (Tables 2 and 4).

Phenanthrene was detected in samples collected at Test field locations TF-7 and TF-8 (Figure 1). No other petroleum-derived chemical was detected in any of the other Test or Control samples collected (Table 2). In light of these results, confirmation samples were collected at the two Test fields. The confirmation samples were collected and analyzed using the same procedures and analytical laboratory applied to samples TF-7 and TF-8. Analytical results for confirmation samples TF-10 and TF-11 are presented in Table 4. None of the eight petroleum-derived chemicals were detected in either of the two confirmation samples (Table 4). A copy of the laboratory report is included in this report as Appendices A and B.

Phenanthrene is known to be produced by the incomplete combustion of fossil fuels and organic materials (HSDB 2016). In fact, phenanthrene has been found to be one of the major organic contaminants produced by domestic wood burning and road traffic (Boström et al, 2002). Phenanthrene produced from combustion of fossil fuels can be found in dust particles in the proximity of roads, chimneys and internal combustion engines (HSDB 2016). Therefore, it is likely that the source of the phenanthrene detected at TF-7 and TF-8 was not the water used to irrigate the crops, but rather the result of the external presence of phenanthrene in the vicinity of the Test fields. In order to analyze this possibility, additional sampling was performed, as described below.

4.1 Confirmation Sampling and Dust Testing Results

During a March 23, 2016 site visit, Dr. Robles observed earth-moving equipment at the agricultural field adjacent to sampling location TF-7. Diesel engines, such as those found in the earth-moving equipment, are known to produce diesel exhaust particles. Diesel exhaust particulates, in turn, are known to contain phenanthrene, which is a major component of diesel exhaust particles (Tsien, Diaz-Sanchez and Saxon, 1997). Given the proximity of the earth-moving equipment to sampling location TF-7, there was concern that the phenanthrene detected in the crop samples could have originated from the diesel exhaust particles released by the operation of the nearby earth-moving equipment.

In an effort to determine if phenanthrene detected in crop samples TF-7 and TF-8 originated from nearby dust/particle emissions from internal combustion engines, confirmation crop samples were taken from the same field as the original test samples, and dust samples were collected from the leaves of the same trees that provided crop samples TF-7 and TF-8. Dust samples were also collected from structures located near the sampling locations. The dust samples were collected by wiping the test surfaces with WetOnes™ moist wipes. The moist wipes containing the surface dust samples were sent to Weck Laboratories for analysis of the nine indicator compounds. Dust sample analytical results are presented in Table 4. None of the indicator chemicals were detected in any of the dust samples, nor were the indicator chemicals detected in the confirmation crop samples.

It should be noted that dust samples were collected on March 23, 2016 and the original crop samples were collected on February 15, 2016. Between the two sampling dates there were several rainy days in the area (U.S. Climate Data 2016). Those rain events likely washed away surface dust from the tree leaves and local structures and, therefore, the dust samples collected on March 23, 2016 do not reflect dust content and dust composition prevalent at the sampling locations on February 15, 2016. Thus, the results of the surface wipe samples from locations TF-7 ad TF-8 do not provide conclusive evidence that phenanthrene was or was not present in the surface dust on February 16, 2016 or prior.

In conclusion, based on the results of the analysis of the original crop samples, the confirmation sampling and the dust test, the petroleum-derived chemicals reportedly found in produced water were not detected in the sampled crops in both the Test and Control samples. The results of this study indicate that the irrigation water indicator chemicals are not reaching the fruit. These results also indicate that blended produced water is safe to use as irrigation on edible tree fruit.

5.0 Oils and Fats

Four of the nine indicator chemicals selected for this study are members of the Polycyclic Aromatic Hydrocarbon (PAH) family. PAHs are found in petroleum products and are also common air contaminants produced by diesel-fueled internal combustion engines (ARB, 2015). Airborne PAHs can be absorbed from the air by plants and stored in their foliage and fruits (Tao, et al., 2004). Especially if those plants have a high oil content (Collins, Fryer and Grosso, 2006).

Since PAHs are known to be ubiquitous in outdoor air (ARB, 2015) and those PAHs can be absorbed from the air by oil-containing fruits (Tao, et al., 2004; Collins, Fryer and Grosso 2006), it is always possible that PAHs detected in the crops actually originated from the absorption of airborne PAHs. The rate of PAH absorption is known to be proportional to the lipid content of the fruit (Collins, Fryer and Grosso 2006). That is, fruits with high oil or fat content have the capacity to attract and retain higher concentrations of lipophilic (fat-loving) chemicals than fruits having lower oil content. In other words, plants with high oil content in their fruits are likely to favor the absorption and accumulation of lipophilic substances from the air. PAHs are highly lipophilic.

Knowing that there is a strong relationship between fruit oil content and PAH absorption, it was necessary to determine the lipid content of the citrus crops in order to assess the potential for chemical absorption from ambient air.

The lipid content of citrus crops was determined by collecting and analyzing fruit samples from the Test and Control fields. The sampling locations were the same as sampling locations used for samples analyzed for indicator chemicals (Figure 1). Citrus crop samples collected in this study were analyzed for total fat and oil content using Analytical Method AOAC Official Method 996.06. Fat and oil content of the Test and Control samples is presented in Table 3. Total fat content of samples collected in this study ranged from 0.01 to 0.27 percent (Table 3). The oil content of both the Test and Control crop samples collected in this study are low and thus, it is possible the low oil content could have contributed to the low absorption of airborne phenanthrene in two citrus samples.

6.0 Conclusions

Produced water is known to contain traces of petroleum hydrocarbons (Table 1). The only chemicals reportedly detected in produced water in Cawelo water supplies were acetone and the petroleum-derived chemicals benzene, toluene, ethylbenzene, xylenes, acenaphthene, fluorene, naphthalene and phenanthrene (Table 1). Since these nine chemicals have been seen in produced water, these same nine chemicals were used in this study as indicator chemicals.

Conclusion:
Mandarins, oranges and lemons irrigated with Cawelo's blended produced water supply safe for consumption.

It should be noted that four of the nine indicator chemicals selected for this study are members of the PAH family. The presence, prevalence and availability of airborne PAHs at the Test and Control fields were not controlled nor measured in this study. Therefore, the total plant absorption of airborne PAHs could not be determined based on the data collected in this study. Realistically then, data collected from this study cannot be used to differentiate the source(s) of any PAHs detected in any given crop sample. In other words, finding PAHs in a crop sample could be indicative of chemical absorption – but no distinction can be made about the source(s) of the detected PAHs. However, the absence of indicator chemicals in the crop samples is clearly indicative of no chemical absorption (from either ambient air or irrigation water).

Test and Control crop sample analytical results are summarized in Tables 2 and 4. Acetone was detected in both Test and Control crop samples. Acetone concentrations detected in both the Test and Control samples were very similar. Based in these results it was concluded that the detected acetone is of natural origin and is not related to the source of irrigation water.

Analytical results for the initial citrus crop samples collected at Test sampling locations TF-7 and TF-8 (Figure 1) revealed the presence of low concentrations of phenanthrene (Tables 2 and 4). No other indicator chemical was detected in any of the other Test or Control samples (Table 2). However, confirmation sampling analytical results for samples TF-10 and TF-11 show no phenanthrene detections. Since, crop samples TF-10 and TF-11 were collected at the same fields where samples TF-7 and TF-8 were collected, these results indicate that phenanthrene is not actually present in the crops at those fields and thus, the phenanthrene detected likely originated from external sources.

Phenanthrene is known to be produced by the incomplete combustion of fossil fuels and organic materials (HSDB 2016). In fact, phenanthrene has been found to be one of the major organic contaminants produced by domestic wood burning and road traffic (Boström et al, 2002). Phenanthrene produced from combustion of fossil fuels can be found in dust particles in the proximity of roads, chimneys and internal combustion engines (HSDB 2016).

In an effort to determine if phenanthrene detected in crop samples TF-7 and TF-8 originated from the nearby internal combustion engine particulate emissions, dust samples were collected from the leaves of the same trees that provided crop samples TF-7 and TF-8. Dust samples were also collected from structures adjacent to the two sampling locations. Dust sample analytical results are presented in Table 4. None of the indicator chemicals selected for this study were detected in the dust samples.

It is not known if combustion emission sources were present in the vicinity of sampling locations TF-7 and TF-8 prior to or during the sampling of the crops. Therefore, the possibility that the detected phenanthrene originated from nearby engine particulate emissions cannot be accepted or discarded at this time.

In conclusion, except for phenanthrene, the indicator chemicals for produced water were either not detected in the sampled crops or were detected at similar concentrations in both the Test and Control samples. The results of this study show that the irrigation water indicator chemicals are either naturally occurring in the sampled crops or are not reaching the crops. As for phenanthrene, confirmation crop sampling and testing revealed no detectable concentrations of phenanthrene in the crops, and therefore the initial test results are deemed to be a false positive and likely a result of contamination from outside sources.

6.1 Limitations

The conclusions presented in this report are professional opinions based solely upon the data described in this report. They are intended exclusively for the purpose outlined herein and the site location and project indicated. This report is for the sole use and benefit of the Cawelo Water District. The scope of services performed in execution of this investigation may not be appropriate to satisfy the needs of other users, and any use or reuse of this document or the findings, conclusions, or recommendations presented herein is at the sole risk of said user.

Given that the scope of services for this investigation was limited, and that conditions may vary between the points explored, it is possible that currently unrecognized water contamination may be present. Should study parameters change, the information and conclusions in this report may no longer apply. Opinions relating to environmental, hydrologic and agricultural health conditions are based on limited data; actual conditions may vary from those encountered at the times and locations where data were obtained. No expressed or implied representation or warranty is included or intended in this report except that the work was performed within the limits prescribed by the client with the customary thoroughness and competence of professionals working in the same area on similar projects.

7.0 Uncertainty Analysis

It is important to specify the uncertainties and limitations of the study for two reasons: (1) to place the conclusions of the report in proper perspective, and (2) to identify key site-related variables and assumptions that contribute most to the uncertainties in the conclusions presented. The objective of this section is to highlight the strengths and weaknesses of the data that are the basis of the report's conclusions and to suggest future studies for collecting the data needed to reduce the uncertainty associated with the conclusions made in the report.

As mentioned in Section 4.0, phenanthrene was the only petroleum-derived chemical detected in two of the Test crop samples. Phenanthrene is not a chemical known to occur naturally in citrus fruits. However, phenanthrene is known to be produced by the incomplete combustion of fossil fuels and other organic materials (HSDB 2016). Phenanthrene, and other members of the PAH family, are also known to settle as dust around combustion emission sources (Tsien, et al., 1997). It is not known if combustion sources were present in the vicinity of sampling locations TF-7 and TF-8 prior to or during the sampling of the crops. Therefore, the possibility that the detected phenanthrene originated from engine particulate emissions cannot be accepted or discarded at this time.

The major limitation of this study is that the indicator chemicals selected for this study are not unique to produced water and are either naturally occurring or common environmental contaminants. The indicator chemicals included in this study were selected because they were the only chemicals detected in blended produced water (Table 1).

In light of the results obtained on this study, future crop samples should be collected away from known sources of petroleum-derived chemicals or combustion products for both the Test and Control sampling locations. In addition, positive results should be followed by confirmation sampling and analysis to determine if those "indicator" chemicals in fact originated in the water supplies or if they are false positives resulting from environmental contamination of the crop samples.

8.0 References

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FIGURE

CAWELO WATER DISTRICT

FIGURE 1
Citrus Crop Sampling & Analysis Report

Test Field Sample Location
Control Field Sample Location